Emulsion Formations

Water production is a major area of concern for crude oil production; this is especially true in steam assisted gravity drainage production. Produced water from the reservoir as well as condensed water from the steam causes the oil to be produced in the form of emulsions.

Emulsions are colloidal dispersions of liquid in another liquid (oil in water), that is, one liquid is microscopically dispersed in the other liquid. Despite the thermodynamic tendency for these liquid in liquid emulsions to separate naturally in order to reduce the interfacial tension between the two liquid phases, the emulsions are formed by kinetic stabilization. Three conditions must exist for kinetic stabilization and therefore, the formation of emulsions

1. An existence of two liquid phases, from a SAGD point of view, this is primarily caused by condensed water from the steam injection
2. Surfactants, either naturally or from chemically injected sources. Surfactants are substances which decrease the surface tension of a liquid.
3. Shearing or mixing, in oil and gas productions, this may be the result of flow through tubes, release of solution gas causing agitation of the fluid, and for SAGD specifically, the result of injected steam agitation of the bitumen.

The most common type of oil emulsions encountered under normal oilfield production conditions is the emulsion in which water droplets is dispersed in oil. During SAGD operations, however, the extracted fluid contains oil dispersed in water; this is generally referred to as a reverse emulsion. Reverse emulsions are generally difficult to break; however, the necessity of breaking these reverse emulsions is crucial due to the limited number of disposal wells available as well as the high steam demand of SAGD operations requiring reuse of the produced water. More importantly, from the perspective of fouling, high efficiency in reverse emulsion breaking will lead to a fewer number of available fouling agents to cause unwanted depositions on the heat exchangers downstream.

**Factors Effecting Emulsion Stability**

From a practical standpoint, emulsion stability is the most critical data for analyzing oil water emulsions. The higher the degree of emulsion stability, the more difficult it is for the oil and water to be separated. Insight into the factors affecting the stability of these oil in water emulsions will provide a greater understanding into the breaking, or de-emulsification of these emulsions. Under normal circumstances, viscous and heavy crude oils (in which SAGD operations is economically viable), the crude oil contains natural emulsifiers which will help to stabilize emulsions by increasing kinetic stability.

Specifically, several factors affect the emulsion stability of reverse emulsions, they are as listed

1. Presence of surfactants which cause the oil to be dispersed in the water as very small droplets.
2. Shearing of the fluid during production, in which the steam flooding causes the generation of smaller droplets, which increase the emulsion stability
3. Higher organic density of the organic compounds in the emulsion increases the stability of the emulsion
4. Presence of fine solids such as clays, sands, or corrosion products injected during production increases the stability of the emulsion

It is noted that contrary to normal water in oil emulsions, temperature of the crude oil does not play a significant factor into the stabilizing the emulsion for reverse emulsions. This is caused by a minor viscosity change in the oil phases with temperature increase and as such, increasing fluid temperature is not a solution to eliminating oil in water emulsions.

**Effect of Surfactants on reverse emulsion stability**

The hydrophilic lipophilic balance (HLB) values of a particular surfactant is a measure of the degree to which the particular substance is hydrophilic (tendency to dissolve in water) or lipophilic (tendency to dissolve in non polar solvents, fats oils and lipids) , as proposed by Griffin in 1949. Surfactants with HLB values between 8 and 18 specifically are determined to be oil in water emulsifiers, which promote the stability of reverse emulsions. This stabilization effect is generally the result of a positive or negative charge induced on the droplets due to the surfactants, resulting in a higher attraction between the polar water molecules and the charge induced droplets.

These reverse emulsion emulsifiers with HLB values between 8 and 18 are sourced from the following potential sources

1. Acidizing/Fracturing stimulations

Acidizing or fracturing stimulations is used in oil wells to increase production. Acid stimulations involve acid injections around the wellbore to eliminate fouling impediments and restore production. Fracturing stimulations is used to increase flow through the formation by creating actual fractures in the formation, allowing for higher flow rate. The surfactants used in these types of production stimulations such as GasPerm 1000 have high HLB values, and may a potential source of emulsifying surfactants.

1. Surfactants from water used during steam injection

Certain surfactants with high HLB values may be injected into the water during certain oil productions to enhance the oil recovery. The additives present in this injection water such as biocides may also lead to oil in water emulsions.

1. Corrosion Inhibitors

Amine corrosion inhibitors that are commonly applied during the production of crude oil may also have high HLB values that can result in reverse emulsions.

**Effect of Crude Oil and Particles on Reverse Emulsion Stability**

Water oil emulsion de-emulsifiers is sometimes applied during crude oil production in order to prevent water oil emulsions, these surfactants generally have an HLB value greater than 6 and although they may prevent water in oil emulsions, they may potentially cause oil in water emulsions. This effect however, depends on the crude oil composition and thus further field tests in this area are needed for optimal oil water separation.

The presence of asphaltene, wax and fine calcium carbonate particles also affects the emulsion stability. Below is an excerpt of the laboratory results conducted by Saudi Aramco on the effect of these particles on emulsion stability. It is noted that water cut is a general term used in oil production to describe the ratio of water produced to the volume of total liquids produced.

An increasing trend in emulsion stability is noticed with increasing calcium carbonate concentrations, and the problem is worsened when the carbonate particles are wetted (coated) by asphaltene.

Table 1: Effect of CaCo3 Particles on ABJF Oil/Water Emulsion stability at 60°C, courtesy of Saudi Aramco Southern Area Laboratories Division

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | Observations of Water separation and emulsion volume | | | | | |
| ABJF Crude with 5% Water cut | | Crude + 50mg/L CaCo3 | Crude + 100mg/L CaCo3 | Crude + 500mg/L CaCo3 | Crude + 50mg/L CaCo3 coated with asphaltene | Crude + 100mg/L CaCo3 coated with asphaltene | Crude + 500mg/L CaCo3 coated with asphaltene |
| Shear strength | | Low shear in shaker for two minutes | | | | | |
| Test Temperature | | 60°C | | | | | |
| Free Water Volume (%) | Settling for 30 minutes | 5 | 4.8 | 5 | 4.5 | 4.5 | 4.5 |
| Settling for 120 minutes | 5 | 5 | 5 | 4.5 | 1.5 | 0.5 |
| After Centrifuging for one minute | Free Water Volume (%) | 5 | 5 | 5 | 5 | 5 | 5 |
| Emulsion Volume (%) | 0 | 0 | 0 | 0.5 | 0 | 0.5 |
| CaCo3 Volume (%) | 0.1 | 0.2 | 0.5 | 0.1 | 0.2 | 0.5 |
| Shear strength | | Medium shear in shaker for ten minutes | | | | | |
| Test Temperature | | 60°C | | | | | |
| Free Water Volume (%) | Settling for 30 minutes | 4 | 4 | 4 | 2 | 1.5 | 1 |
| Settling for 120 minutes | 4.5 | 4.5 | 4 | 2.5 | 2 | 2 |
| After Centrifuging for one minute | Free Water Volume (%) | 5 | 5 | 5 | 5 | 5 | 5 |
| Emulsion Volume (%) | 0 | 0 | 0 | 1 | 1 | 1 |
| CaCo3 Volume (%) | 0.1 | 0.2 | 0.5 | 0.1 | 0.2 | 0.5 |

**Effect of shearing in reverse emulsion stability**

Water in oil emulsions and reverse emulsions share the same characteristic that higher shear strength results in a more stable emulsion. The following lab information is synthesized from shearing tests conducted by Saudi Aramco. An increasing trend of emulsion stability is noticed with the increasing shear strength (less settling is observed).

Table 2: Effects of Water cut and shear on ABJF Oil/ Water Emulsion Stability at 60°C, courtesy of Saudi Aramco Southern Area Laboratories Division

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | Observations of Water separation and emulsion volume | | | | | |
| Water Cut (%) | | 5 | 10 | 15 | 20 | 25 | 30 |
| Shear strength | | Low shear in shaker for two minutes | | | | | |
| Test Temperature | | 60°C | | | | | |
| Free Water Volume (%) | Settling for 30 minutes | 4.0 | 10 | 15 | 20 | 23 | 26 |
| Settling for 120 minutes | 4.5 | 10 | 15 | 20 | 25 | 30 |
| After Centrifuging for one minute | Free Water Volume (%) | 5.0 | 10 | 15 | 20 | 25 | 30 |
| Emulsion Volume | 0 | 0 | 0 | 0 | 0 | 0 |
| Shear strength | | Medium shear in shaker for ten minutes | | | | | |
| Test Temperature | | 60°C | | | | | |
| Free Water Volume (%) | Settling for 30 minutes | 3.0 | 8.0 | 10 | 15 | 15 | 18 |
| Settling for 120 minutes | 4 | 9 | 13 | 18 | 20 | 25 |
| After Centrifuging for one minute | Free Water Volume (%) | 4 | 9 | 14.5 | 19 | 20 | 25 |
| Emulsion Volume | 2 | 3 | 3.5 | 2 | 7 | 7 |

**Breaking Reverse emulsions**

Many different methods are employed to breaking oil in water emulsions. One such method patented by Jacques et al which involving the use of a “dispersible terpolymer that consists of acrylamide, acrylic acid (or its salt derivatives) and alkylacrylamide or alkylacrylate or alkylmethacrylate; or copolymers consisting of acrylamide and alkylacrylamide or alkylacrylate or alkylmethacrylate alone or in combination with a cationic species” will be investigated.

This method of breaking reverse emulsions consists of the following steps

1. Treating the emulsion with an ionic chemical to neutralize the charge of the oil droplets dispersed in the water. This ionic chemical is a cationic polymer (positive in charge) which can be selected from the following
   1. melamine-formaldehyde resin
   2. polyepichlorohydrins
   3. poly-3-methacrylamidopropyltrimethylammonium chloride and copolymers with acrylamide
   4. poly-2-methacrylatoethyltrimethylammonium chloride and copolymers with acrylamide,
   5. diallyl dimethylammonium chloride and copolymers with acrylamide
2. The addition of a water soluble copolymer (a water dispersible hydrophobic ally functionalized copolymer), consisting of a water soluble and oil soluble (hydrophobic) portion. This copolymer is made of the following two monomers
   1. One monomer (this is the hydrophobic monomer) consisting of 0.1-10 molar percentage of alkylacrylamide and alkyl(meth) acrylate with an akyl group with 4-20 carbon atoms
   2. The other monomer (this is the water soluble monomer) consisting 90-99.9 molar percentage of either acrylic acid or salts of acrylic acid
3. Allowing for the particles to separate by gravity, this is usually done by a skim tank in SAGD operations.

Alternatively, a terpolymer can be used in place of a copolymer.

1. Treating the emulsion with an ionic chemical to neutralize the charge of the oil droplets dispersed in the water. This ionic chemical is a cationic polymer (positive in charge) which can be selected from the following
2. melamine-formaldehyde resin
3. polyepichlorohydrins
4. poly-3-methacrylamidopropyltrimethylammonium chloride and copolymers with acrylamide
5. diallyl dimethylammonium chloride and copolymers with acrylamide
6. The addition of a water soluble terpolymer (a polymer derived from three monomers), consisting of a water soluble portion an anionic water soluble portion, an an oil soluble (hydrophobic) portion. This terpolymer is made of the following three monomers
7. 0.1-10 molar percentage of one monomer (this is a hydrophobic monomer) consisting of alkylacrylamide or alkyl(meth) acrylate with an akyl group with 4-20 carbon atoms
8. 5-40 molar percentage of one monomer (this is the water soluble monomer) consisting of either acrylic acid or methacrylic acid
9. 50-94.9 molar percentage of the last monomer (the other water soluble monomer), an acrylamide monomer.
10. Allowing for the particles to separate by gravity.

These steps are discussed in greater detail below

**Treatment with a cationic polymer for negative charge reduction**

The first step involves the use of the treatment of the emulsion with a cationic polymer. The suitable cationic additives are mentioned above. In reverse emulsions, the oil droplets and other contaminants that cause fouling in various equipments carry a negative charge. The addition of cationic polymers will effectively neutralize the charge on these oil droplets or contaminants. To ensure complete neutralization of this negative charge, an amount of cationic polymer that is sufficient to neutralize all the negative charges on the droplets with perhaps even a low level of residual cationic charge is desired. The final state of this step results in oil droplets that are neutral or with a slight cationic surface charge for the next step of this process.

**Treatment with an effective amount of hydrophobically functionalized water soluble polymer**

The alkyacrylamide or akylacrylate used in this step have limited solubility in water and show a tendency to react very strongly with oil droplets in the waste water. The chain length on the alkyl group of these hydrophobic monomers is related to its insolubility and a carbon chain length of ranging from 6-20 is preferably used. Additionally the amount of hydrophobic group in the polymer necessary for oil water treatment decreases with increasing chain length, for example less octylacrylamide is needed for the same function as alkyacrylamide.

Terpolymers that consist of an acrylamide, a hydrophobic monomer (as descrbied earlier) and salts of acrylic acid can also be used. The desired characteristic is to have a hydrophobic monomer that decreases the solubility of the polymer which will enable the rapid interaction with the dispersed oil droplets in the water. The amount of this hydrophobic will need to be increased for example, if say there is a high presence of charged groups (such as carboxylic acids).

The function of these hydrophobic groups greatly improves the breaking of oil water emulsions with respect to polymers without hydrophobic groups. The emulsified oil droplets in water generally carry a negative surface charge, this is the basis of stabilization of emulsions, that is, emulsions are stabilized by the electrostatic charge repulsion between the oil droplets, keeping them dispersed in the water. The first step of application (adding cationic polymer) of breaking reverse emulsions effectively reduced the charge on these oil droplets, eliminating the electrostatic repulsion (ie. decreasing the emulsion stability greatly). As such, the oil droplets will start to approach each other and coalesce, eventually the large agglomeration (otherwise known as flocculation) of oil occurs and this floc of oil (and other contaminants) will begin to float to the top of the emulsion. The larger the flocculation, the faster the rate at which they will rise to the top of the water. The addition of the hydrophobically functionalized polymer then attaches to the oil droplets and the resulting polymer bridging accelerates the floc formation. The hydrophobically functionalized polymers can attach to the oil by means of coulombic attraction (attraction of opposite charges), hydrogen bonding and by hydrophobic attraction to the oil droplets. After a prescribed amount of time, the oil droplets and polymer separate into distinct layers from the water and can then be skimmed off in a skim tank.

The use of a hydrophobically functionalized polymer as opposed to conventional polymers without hydrophobic monomer groups has been proven in laboratory tests to greatly improve the breaking of reverse emulsions. Results indicated an improved ability in oil breaking with significantly less concentration of remaining oil as opposed to treatment with a polymer without a hydrophobic group. As well, the formed floc particles were more difficult to redisperse back into the water with additional agitation.